COAL/RESID COPROCESSING OVER EQUILIBRIUM HYDROTREATING CATALYST

R. J. Torres-Ordonez
S. G. Kukes
Amoco Oil Company
Amoco Research Center
P. O. Box 3011
Naperville, Illinois 60566

W. A. Leet
Amoco Oil Company
P. O. Box 160
Casper, Wyoming 82601

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ABSTRACT

Resid and a 10% coal/resid mixture were hydroprocessed in a flow unit at 760-790°F over an equilibrium commercial hydrotreating catalyst. Coal addition resulted in improvements in both hydrodemetallization activity and Ramscarbon conversion; however, hydrodesulfurization activity remained the same. The addition of 10% decanted oil to the coal/resid feed considerably improved coal conversion.

INTRODUCTION

Extensive information on coal/petroleum resid coprocessing is available in the open literature, both for experiments in batch units and in continuous bench scale units. Oelert (1) provides a review of the background technology and discusses research and development in various coprocessing schemes. Many of these coprocessing studies claim synergisms, or benefits relative to resid hydroprocessing or coal liquefaction. Among these synergisms are:

a) Improved unit operability due to the formation of less solids or coke (2). This benefit may also allow unit operation at higher temperatures than those possible with just resid hydroprocessing.
b) Enhanced metals removal (3-6), which has been attributed to the preferential deposition of the metals on the coal solids instead of on the catalyst (7). This benefit may allow the processing of resids with high metal contents (8).
c) Improved heteroatom removal (4,5,9) (i.e., sulfur, nitrogen and oxygen).
d) Increased distillate yields (4,9,10).
e) Reduction of overall hydrogen requirement (relative to coal liquefaction) with the use of higher H-content resid.

The goal of the current work is to verify and quantify synergisms for the coprocessing of coal and resid over commercial equilibrium hydrotreating catalyst in a continuous bench scale flow unit. The specific objectives are (a) to evaluate the effects of process variables, such as temperature and solvent addition, on coal/resid conversion and product properties, and (b) to determine the impact (if any) of coprocessing on catalyst activity maintenance and catalyst life.

EXPERIMENTAL

Feed Properties

Hydroprocessing experiments were performed on a resid and a blend of this resid with Illinois No. 6 coal, with or without decanted oil. The properties of the above feeds are shown in Table 1.

Reaction Conditions

The hydroprocessing experiments were conducted in an upflow high-pressure unit which contains two 1-liter Autoclave reactors in series. Catalyst baskets, each filled with 60 cc of equilibrium hydrotreating catalyst, were placed in both reactors. To prevent elutriation, the catalyst was covered with 10 cc of 3 mm glass balls and 1/4 inch of glass wool. Table II gives the experimental conditions for the following four tests:

Test No. 1	Hydroprocessing of Resid
Test No. 2	Coprocessing of 10% Coal + 90% Resid
Test No. 3	Hydroprocessing of 10% DCO + 90% Resid
Test No. 4	Coprocessing of 10% Coal + 9% DCO + 81% Resid

Product Analysis

Products from the hydroprocessing runs were analyzed for tetrahydrofuran (THF) and hexane insolubles. Samples were also subjected to Shell hot filtration tests (SHFT) to determine "solids" concentration. In this test, the sample is filtered through Whatman 50 paper at about 200°F; if the sample does not filter after one hour, 10-20 psi nitrogen is applied. The solids are then washed with hexane (four 50 ml washes for 10 g sample) before final filtration; the recovered solids are termed the SHFT solids. The resulting SHFT filtrate was then analyzed for elemental composition (C, H, N, S, O), metals (Ni, V) and Ramscarbon contents (Tables III and IV). Product gas samples from selected runs were also analyzed by gas chromatography to determine the total material balance closure, which averaged 93% due to plugging problems.

RESULTS AND DISCUSSION

Resid and Coal/Resid Coprocessing Without DCO (Tests No. 1 and No. 2)

Coal addition considerably improved the hydrodemetallization (HDM, calculated as shown in the appendix) of resid at 760-790°F (Figure 1). The HDM benefit from coal addition became smaller at higher temperatures.

The Ramscarbon conversion (HDC, calculated as shown in the appendix) also increased with coal addition, as shown in Figure 2. It is possible that adsorption of asphaltenes (or Ramscarbon to some degree) by unconverted coal resulted in this apparent increase in Ramscarbon conversion. As with HDM, the HDC benefit with coal addition became smaller at higher temperatures.

The hydrodesulfurization (HDS, calculated as shown in the appendix) was not affected by coal addition, as shown in Figure 3. Nitrogen and oxygen removal were low due to the high space velocity and low hydrogenation activity of the equilibrium catalyst.

The THF insolubles (See Table III) were used to estimate coal conversion (see appendix). Within experimental error, the coal conversion remained relatively constant from 760 to 780°F at a minimum of 46-48% to a maximum of 60-62% (see Table V). These conversions were lower than those obtained in the liquefaction of Illinois No. 6 (with coal liquids as solvent) under comparable coal liquefaction conditions (11). The lower coal conversion during coal/resid coprocessing may be due to the poor solvent quality of the petroleum resid.

Resid and Coal/Resid Coprocessing With DCO (Tests No. 3 and No. 4)

Initially a mixture of 90% resid and 10% decanted oil was hydroprocessed for about 120 hours. Then 10% coal was added to the feed and the coal/resid/DCO mixture was hydrotreated for 180 hours. At the end of this run, the coal was removed and the (resid+DCO) was processed for 120 hours to check the baseline. Figures 4-6 show HDM, HDC, and HDS of liquid products as a function of the time on stream. As in the coprocessing without decanted oil, the addition of coal resulted in increases in HDM and HDC (Figures 4 and 5); HDS was only slightly improved (Figure 6). Regression lines (the solid lines in Figures 4-6) indicated that the equilibrium catalyst was undergoing further deactivation. The addition of coal did not affect this deactivation rate. Catalyst activity for HDM drastically decreased two days after coal was removed from the feed. We do not have an explanation for this unusual observation.

The addition of DCO improved coal conversion, as seen in Table VI. For hydroprocessing at 780°F, coal conversion increased from a minimum of 46% (maximum of 60%) without DCO to a minimum of 66% (maximum of 80%) with DCO addition to the coal/resid mixture.

CONCLUSIONS

The addition of decanted oil to a coal/resid mixture resulted in improved coal conversion. When 10% Illinois No. 6 coal was coprocessed with resid, both metals and Ramscarbon removal from resid were increased, with or without decanted oil. Increases in apparent resid Ramscarbon removal with coal present can be due to heavy molecule adsorption by unconverted coal. Sulfur removal, however, was not affected by coal addition.

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Table I. Hydroprocessing Feed Properties

Feed No.	Composition, % MAF Resid	Coal	DCO	%THF Solids	%SHFT Insol	% C	% H	% N	% S	% O	% Rams-carbon	ppm Ni	ppm V	ppm Fe
1	100	0	0	N.D.[1]	1.6	84.65	10.35	0.45	4.70	0.40	17.7	54	215	21
2	0	0	100	N.D.	N.D.	90.75	7.22	0.17	1.68	1.48	9.4	0	0	0
3	0	100	0	91.06[2]	N.D.	77.31[3]	5.13[3]	1.43[3]	3.93[3]	12.20[3]	N.D.	15	32	15,300
4	90	0	10	N.D.	1.43	85.26	10.04	0.42	4.40	0.51	16.9	49	194	19
5	90	10	0	9.11[4]	11.4	83.92	9.83	0.55	4.62	1.58	25.0	50	197	1549
6	81	10	9	9.11[4]	11.3	84.47	9.55	0.52	4.35	1.68	20.3	45	177	1547

[1] N.D. = not determined
[2] 98.0% MF coal
[3] Wt% MAF (coal contained 1.14 wt% ash and 7.1 wt% moisture)
[4] 9.8% MF coal

Table II. Hydroprocessing Conditions

	1st Stage Reactor	2nd Stage Reactor	Reactor Train
Average Feed Rate, g/hr	206	206	206
Equilibrium Catalyst			
Catalyst Volume, cc	60	60	120
Catalyst Weight, g	65	65	130
WHSV, 1/hr (based on fresh catalyst)	7.4	7.4	3.7
WHSV, 1/hr (based on equil. catalyst)	3.2	3.2	1.6
Effective Reactor Volume*, cc	282	282	564
Residence Time, hr	1.37	1.37	2.74
LHSV, 1/hr	3.4	3.4	1.7
Pressure, psig	2500	2500	2500
Hydrogen Flow Rate			
SCFH	10	10	10
SCFB	7700	7700	7700
Agitator Speed, rpm	1650	1000	

*Effective reactor volume calculated assuming 10% gas holdup and 0.2 cc/g spent catalyst pore volume, i.e.,
Effective Volume = Total Liquid Volume Outside Catalyst Pores x (1-gas holdup fraction) + Catalyst Pore Volume
= 300 (1 - 0.1) + 60 (0.2) = 282

TABLE III: Analysis of Products from Resid and Coal Resid Hydroprocessing

Test No.	Feed Comp[1] %Coal	% DCO	Temp (°F)	Time (hr)	%THF Insol.	% SHFT Solids	% C	% H	% N	% S	% O	% Rams-carbon	ppm Ni	ppm V	ppm Fe
1	0	0	780	63	0.14[2]	5.60	85.86	11.14	0.41	2.31	1.06	10.6	14	53	2
1	0	0	770	136	0.33[2]	3.67	85.63	10.90	0.44	2.57	1.06	12.5	22	78	2
1	0	0	760	155	0.21[2]	4.07[4]	85.63	10.77	0.47	2.83	1.29	13.4	29	105	2
1	0	0	790	179	0.17[2]	5.47	86.07	11.26	0.37	1.97	1.10	9.3	8	31	2
2	10	0	780	255	4.44[3]	13.96[5]	85.65	10.67	0.49	2.54	1.48	13.0	15	38	2
2	10	0	770	283	2.92	17.05	85.42	10.69	0.48	2.71	N.D.	13.8	19	53	2
2	10	0	770	297	5.93	N.D.	85.10	10.43	0.51	3.05	1.41	14.9	24	74	2
2	10	0	760	309	5.13	N.D.	85.31	10.68	0.46	2.95	1.63	13.0	20	62	2
2	10	0	760	325	3.76	14.87	85.04	10.61	0.48	3.06	1.09	14.4	24	74	2

[1] %Coal + %DCO + %Resid = 100%
[2] Average THF insolubles for entire time on stream at the given temperature.
[3] Average of THF insolubles at 255 and 270 hours.
[4] SHFT solids at 165 hours.
[5] SHFT solids at 270 hours.
N.D. = not determined.

TABLE IV. Analysis of Products from Resid and Coal/Resid Hydroprocessing with Decanted Oil[1]

Test No.	Feed Comp[2] % Coal	Feed Comp[2] % DCO	Temp. (°F)	Time (hr)	%THF Insol.	%SHFT Solids	%Hexane Insol.	Filtered Product Quality % C	% H	% N	% S	% Rams-carbon	ppm Ni	ppm V	ppm Fe
3	0	10	780	38	N.D.	2.39	4.93	86.18	10.67	0.45	2.37	12.5	24	73	2
3	0	10	780	62	N.D.	2.45	6.85	86.07	10.68	0.42	2.22	11.4	21	64	2
3	0	10	780	73	0.62	2.24	9.75	85.84	10.71	0.42	2.32	11.4	21	65	2
3	0	10	780	84	N.D.	2.42	9.85	85.34	10.67	0.40	2.39	11.6	23	74	2
3	0	10	780	106	0.50	2.04	9.41	86.46	10.70	0.42	2.38	11.5	22	70	2
4	10	9	780	128	N.D.	6.90	N.D.	86.35	10.56	0.45	2.18	12.0	15	42	2
4	10	9	780	152	3.77	10.61	N.D.	86.33	10.47	0.42	2.35	11.9	15	34	1
4	10	9	780	175	3.36	8.58	14.11	85.99	10.33	0.43	2.42	12.0	17	35	1
4	10	9	780	196	N.D.	10.21	14.92	86.16	10.45	0.49	2.57	13.2	18	42	1
4	10	9	780	216	2.57	10.08	15.43	86.18	10.35	0.43	2.49	12.6	20	44	1
4	10	9	780	239	N.D.	9.72	14.71	86.13	10.43	0.46	2.54	13.7	22	44	15
4	10	9	780	263	3.29	9.49	14.15	85.48	10.43	0.40	2.45	12.8	16	34	1
4	10	9	780	287	N.D.	11.00	15.72	86.03	10.36	0.41	2.65	13.6	22	48	1
3	0	10	780	310	N.D.	3.19	N.D.	85.89	10.39	0.44	3.08	13.3	27	83	1
3	0	10	780	333	N.D.	2.45	N.D.	86.06	10.55	0.42	2.89	13.0	24	74	0
3	0	10	780	357	0.59	2.03	11.51	85.96	10.52	0.43	3.07	13.4	34	126	2
3	0	10	780	381	N.D.	1.89	11.40	86.02	10.45	0.42	3.09	13.3	35	126	2
3	0	10	780	405	0.60	2.08	11.29	86.00	10.30	0.41	3.13	13.5	35	127	2
3	0	10	780	429	N.D.	1.74	N.D.	85.74	10.34	0.41	3.11	13.4	34	127	2

1 No oxygen analyses were performed for this set of runs.
2 %Coal + %DCO + %Resid = 100%

Table V. Conversion of THF Insolubles

Temperature, °F	%THF Insolubles in Product		% Coal Conversion	
	Resid	Resid + Coal	Minimum	Maximum
760	0.2	4.4	47	61
770	0.3	4.4	48	62
780	0.1	4.4	46	60

*THF insolubles in coal/resid feed = 9.1%
Ash in coal/resid feed = 1.1%

TABLE VI. Hydroprocessing at 780°F

Test	Feed	Time (hr)	%HDM	%HDC	%HDS	% SHFT Solids	% Coal Conversion	
							Minimum	Maximum
1	Resid	63	77	44	54	6	--	--
2	Resid+Coal	255	82	56	53	14	46	60
3	Resid+DCO	62	66	35	51	2	--	--
4	Resid+DCO+Coal	263	80	44	50	9	66	80

FIGURE 1.
COAL/RESID COPROCESSING – HYDRODEMETALLIZATION

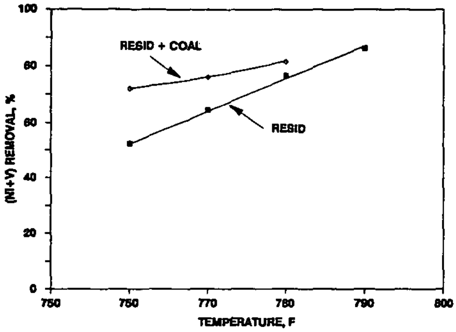


FIGURE 2.
COAL/RESID COPROCESSING – RAMSCARBON CONVERSION

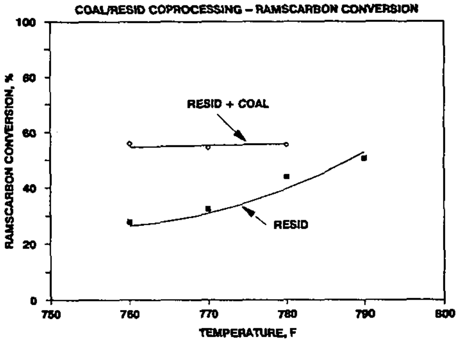


FIGURE 3.
COAL/RESID COPROCESSING – HYDRODESULFURIZATION

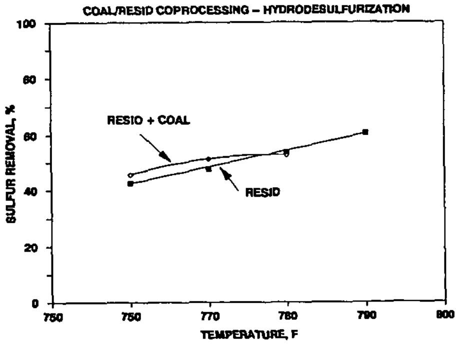


FIGURE 4.

COAL/RESID COPROCESSING WITH DCO AT 780 F – HYDRODEMETALLIZATION

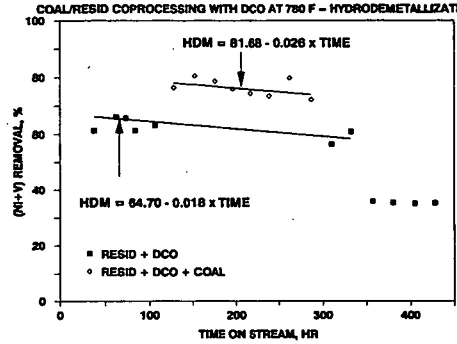


FIGURE 5.

COAL/RESID COPROCESSING WITH DCO AT 780 F – RAMSCARBON CONVERSION

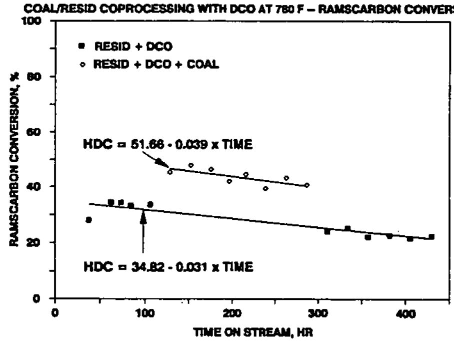
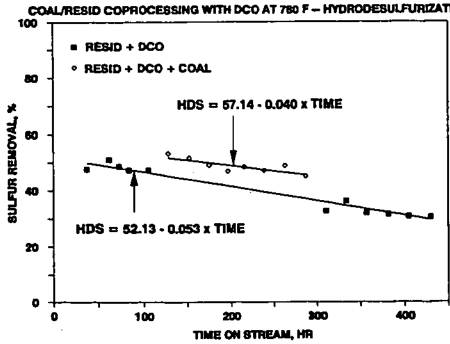


FIGURE 6.

COAL/RESID COPROCESSING WITH DCO AT 780 F – HYDRODESULFURIZATION



APPENDIX

Conversion Calculations

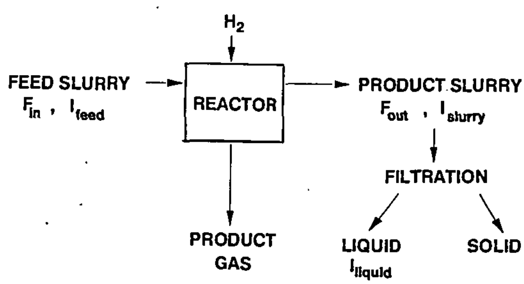
Figure A-1 shows the block diagram for the reactor system, along with the feed and product streams, and their analysis. The analytical results reported in Tables III and IV were used to calculate the following levels of conversion or removal in the liquid product (assuming no product loss on filtration):

% Conversion or Removal of Component I (HDI):

$$\{[F_{in}I_{feed} - F_{out}(1 - \text{SHFT solids fraction})I_{liquid}]/[F_{in}I_{feed}]\} \times 100$$

where for hydrodemetallization (HDM), I = ppm (Ni+V); for Ramscarbon conversion (HDC), I = % Ramscarbon; and for hydrodesulfurization (HDS), I = % Sulfur. F_{out}/F_{in} represents the material balance which may be calculated based on the total material (0.93), or based on a forced carbon balance (0.99). In Figures 1-6, F_{out}/F_{in} = 0.99 is used; the use of F_{out}/F_{in} = 0.93 gives values that are at most 10% higher.

Figure A-1.
Material Balance Block Diagram for Flow Unit



Coal conversion was estimated by conversion to THF solubles. It was assumed that the coal-derived THF insolubles (THF) is given by the difference between the THFI in the coprocessing product and the THFI in the resid hydroprocessing product (weighted by its fraction in the coprocessing feed), i.e.,

Coal Conversion to THF Solubles:

$$1 - \{[(\text{THFI-Ash})_{\text{coproc product}} - 0.9\text{THFI}_{\text{resid run}}]/(\text{THFI-Ash})_{\text{coproc feed}}\}$$

The ash deposition on the catalyst could not be evaluated because the catalyst was severely coked and could not be recovered for analysis. Two approaches were used to estimate the ash levels in the coprocessing product. In the first, it was assumed that all of the ash deposited in the catalyst so that $\text{Ash}_{\text{coproc product}} = 0$; the calculated coal conversion is then a minimum. In the second, it was assumed that no ash deposited in the catalyst so that $\text{Ash}_{\text{coproc product}} = \text{Ash}_{\text{coproc feed}} = 1.14\%$; the calculated conversion is then the maximum possible.